REVIEW AND STATUS OF LOW-TEMPERATURE TAR INVESTIGATIONS OF THE BUREAU OF MINES

BY BUREAU OF MINES STAFF

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REVIEW AND STATUS OF LOW-TEMPERATURE TAR INVESTIGATIONS OF THE BUREAU OF MINES[1/]

by

Bureau of Mines Staff

INTRODUCTION AND SUMMARY

From the time of its establishment in 1910, the Federal Bureau of Mines has studied the carbonization of coal, and a considerable part of this effort has been devoted to investigations in the so-called low-temperature carbonization range, 450° to 700° C., in which there is minimum decomposition of primary products and maximum yield of liquids - a yield two to threefold the amount produced in high-temperature carbonization at 900° to 1,200° C. The solid residue, char, or coke, produced in low-temperature carbonization is 70 to 80 percent of the coal charged and may be used directly as a smokeless fuel or for blending with coals to produce metallurgical coke.

Although some thought was given to the use of tar and to the illuminating value of gas derived from low-temperature carbonization, the main emphasis in early work of the Bureau of Mines was on the preparation of smokeless fuel, especially for home use. For example, a carbonizer was designed and operated for making char and briquets from North Dakota lignite without recovery of by-products; however, the shortage of high-temperature coal-tar products in the United States during World War I had already indicated the potential usefulness of low-temperature tar.

At present little, if any, premium could be obtained for the heat units in low-temperature cokes or chars as compared with those in the original coal. In most areas of the United States large volumes of coke or char produced by low-temperature carbonization would have to be used as fuel in electric powerplants and would command prices no higher than those reflecting actual heating value. Interest in smoke abatement and the passage of laws aimed at mitigation of atmospheric pollution have created local markets for smokeless solid fuels at a premium price; however, with rapid extension of pipeline networks carrying low-cost, convenient, gaseous fuels, these markets are limited. Profitable utilization of the tar will be vital to the economic success of low-temperature carbonization.

The relatively greater success of low-temperature carbonization abroad has depended not only on greater demand for tar but also on larger markets for

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prepared solid fuels at premium prices. Recent increased use and processing of petroleum products, on the continent and in the British Isles, indicate a shrinking market for premium heat units in solid fuels, even in those countries.

In the United States development of low-temperature carbonization has been slow, despite great expenditure of effort by industry and Government. A market for the rather special tar products, however valuable they may prove to be in the future, is still to be created. The objective of Bureau research and development in this field is to aid in establishing a low-temperature carbonization industry that would contribute to better utilization of our coal resources. One of the main tasks in achieving this goal is to learn more about (1) the nature of low-temperature tar, (2) the effects of rank of coal as well as carbonization conditions on the composition of this tar, and (3) methods for converting tar fractions or the whole tar into marketable products. The approach therefore emphasizes the application and adaptation of modern analytical, separative, and upgrading techniques to low-temperature tars. Thus, average properties of tar fractions obtained by physical and/or chemical separations are determined, individual tar constituents are identified by comparison of their physical and chemical properties with those of known compounds, and methods are studied for chemically modifying certain fractions, particularly the higher boiling ones, to obtain simpler, more useful products.

The first bulletin published by the Bureau of Mines in 1910 concerned volatile matter in coal and furnished tar yields obtained from four coals carbonized at 500° to 900° C. Simple analyses of tars produced by carbonizations at 500°, 600°, and 700° C. were part of the Bureau of Mines-American Gas Association (BM-AGA) survey program at Pittsburgh until 1949, when carbonizations at these temperatures were discontinued. Between 1926 and 1929 a series of papers was published on the detailed composition of light oils and tar obtained by low-temperature carbonization of a noncoking coal from Utah. This work was, of course, limited by the methods of analysis available at that time.

Revived interest in the nature of low-temperature tars dates from the carbonization work begun in 1937 by the late V. F. Parry at the Bureau's Golden, Colo., Station. This work was transferred to Denver in 1949. Studies of the carbonization characteristics of lignites have been carried on also at the Grand Forks, N. Dak., Station since 1951. In 1955 a laboratory devoted exclusively to analysis, characterization, and upgrading of low-temperature tar was established at the Morgantown, W. Va., Station.

At present the Pittsburgh Station is engaged in small-scale pilot-plant work on producing and treating primary tar. Research on the structure and reactivity of coal and on physical and chemical methods of analysis at the Pittsburgh and Bruceton laboratories is contributing to our knowledge of low-temperature tars, just as information on these tars will aid in better understanding of the properties of coal. The Denver Station has been working on gross characterization of tar obtained from western coals and its variation with processing, transportation, and storage conditions. The Grand Forks Lignite Experiment Station is studying the detailed composition of low-temperature tar produced from lignite; the Morgantown Station is working on the composition of bituminous-coal tar and its chemical upgrading.

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Current commercial interest in low-temperature tar and its potentialities as a source of chemicals and specialty fuels has prompted this review of the present program and status of Bureau work on low-temperature tar.

WORK AT CENTRAL EXPERIMENT STATION, PITTSBURGH, AND AT BRUCETON, PA.

The early work (1-22)[2/] of A. C. Fieldner, J. D. Davis, R. L. Brown, V. F. Parry, E. E. Schneider, and their coworkers at the Central Station was aimed at obtaining general information on the yields and composition of low-temperature tars from certain American and foreign coals.

In later work, as part of the BM-AGA survey of the carbonizing properties of American coals, tars from coals carbonized at 500° to 1,000° C., at 100° intervals, were analyzed. Bituminous coals of all ranks, subbituminous, and lignitic coals (21) were carbonized. Although these investigations give data for analyses of tar at all temperatures, the main interest of the BM-AGA survey was in producing metallurgical coke, or high-temperature carbonization. Thus, the effects of process variables were determined only for the high-temperature tars. A general characterization of the tars from all carbonization temperatures was made so that the effect of temperature on the quality of products could be determined. The tar analyses included determination of specific gravity, benzene insoluble (free carbon), distillation range, proximate and ultimate analyses, and contents of acids, bases, neutral oils, olefins, aromatics, paraffins, naphthenes, naphthalene and anthracene salts, and pitch. Generally, the nature of coal tar is influenced appreciably by the composition of the coal carbonized when carbonization is effected at low temperatures, but under high-temperature carbonizing conditions the effect of coal composition is largely eliminated by the thermal decomposition of those compounds that were responsible for the characteristic differences in the tars produced at lower temperatures. For low-temperature tars the acid content was related to the oxygen content of the coal; the aromatic and paraffinic and naphthenic content was related to the hydrogen content of the coal; the base content was not closely related to the nitrogen content of the coal; and, except for high-sulfur coals, the sulfur content was not related to the sulfur content of the coals.

The BM-AGA survey provides comparable data on the yields and properties of tar from individual coals from most coal-producing sections of the country. This information is valuable when coals are selected for specific purposes. The average yields for a number of carbonization tests at 500° C. for coals of various ranks are shown in table 1. The yields of tar and tar constituents were found to be strongly influenced by the rank of the coal and reached a maximum in high-volatile A coals.

Current experimental work at this station on low-temperature tar is directed toward determining the effect of secondary thermal treatment of uncondensed tar vapors on tar properties. This work is part of the study of mechanism and kinetics of coal carbonization. In the first phase of this investigation tar produced in a fluidized carbonizer at 490° C. was collected

2/ Underlined numbers in parentheses refer to items in the bibliography at the end of the report.

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and analyzed. A tar yield of 45.9 gallons per ton of coal was obtained as compared with 26.1 gallons per ton from the same coal carbonized by the BM-AGA fixed-bed method at 500° C. Tar from the fluidized-bed carbonization contains less tar oil in the boiling range 0° to 235° C., about the same amount in the range 235° to 350° C., and considerably more pitch than the tar produced in the BM-AGA apparatus. The BM-AGA tar contained 9.4 gallons per ton of pitch, whereas the fluidized carbonizer tar contained 31.8 gallons of pitch. In fixed-bed carbonization the gases from the plastic layer pass through the newly formed coke, where the larger and/or more reactive molecules, pitch progenitors, probably are retained and coked; whereas in fluidized carbonization the evolved tar vapors are swept out very quickly. In the next phase of this investigation the tar vapors from the fluidized carbonizer will pass through a thermal cracker at 600°, 700°, and 800° C. in a study of the effect of thermal treatment on tar properties.

TABLE 1. - Average yields of tar and tar constituents in carbonizations at 500° C. (gallons per ton, moisture- and ash-free basis)

Rank	Number of coals	Tars	Acids	Bases	Neutral oils	Olefins	Aromatics	Paraffins and naphthenes	Residues
Bituminous:									
Low-volatile...	10	5.1	0.32	0.04	2.28	0.14	1.61	0.53	2.49
Medium-volatile	7	11.0	.96	.10	4.76	.30	2.70	1.77	5.12
High-volatile A	29	26.3	4.72	.38	10.76	.99	5.36	4.41	10.43
High-volatile B	3	20.8	5.75	.32	9.72	1.31	4.93	3.49	8.35
High-volatile C	2	18.1	5.54	.47	8.44	1.35	4.59	2.50	7.80
Subbituminous ...	2	11.0	3.65	.35	6.54	1.11	3.13	2.30	4.20
Lignite	1	4.5	.39	.10	2.34	.30	1.46	.58	1.67

A recent publication (23) has summarized the results of Fischer-Schrader low-temperature-carbonization assays of some 400 samples of coals originating in many coal-producing States of the United States, including Alaska, and in British Columbia, Canada.

Experiments have been made at the Bruceton Station on the hydrogenation reactions of a topped low-temperature tar, 91.4 percent of which boiled above 325° C., at 1 atmosphere. Reaction without a catalyst at 475° C., 7,500 p.s.i. of hydrogen, and 2-1/2 hours of residence time converted 45 percent of this material to oils boiling below 325° C. and 16 percent to hydrocarbon gases (C_1 to C_5). The yield of tar acids boiling under 250° C. in the oils was 4 percent of the feed, and the yields of aromatics, naphthenes, and paraffins were each less than 1 percent. In experiments with catalysts mechanical difficulties were encountered, but there was evidence of a considerably increased rate of degradation of asphaltenes to oils in those runs where catalysts were present.

Recent applications at the Bruceton Station of low-voltage mass-spectra techniques to identification of components in tar-acid mixtures have indicated that this may be a very useful tool in the rapid characterization of tar acids and aromatic hydrocarbons in low-temperature tars. Work in this field is proceeding.

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LOW-TEMPERATURE TAR INVESTIGATIONS AT DENVER EXPERIMENT STATION

Because of the economic importance of utilizing the great reserves of low-rank coals in the West Central States, a major part of the effort of this station was directed for many years toward the storage, drying, combustion, and carbonization of the low-rank coals. As one result of this effort, highly efficient fluid and entrained-bed processes were developed for drying and carbonizing lignite; and as an outcome of these and related developments, the generation of electrical energy from solid fuels for primary aluminum production first became an economic reality, as evidenced by operations of the Texas Power & Light Co. at Rockdale, Tex.

The possibility of introducing a carbonization stage ahead of the combustion process and using the finely divided char from this as the fuel for power generation was envisioned very early in the development. For such a system to be economic, the return from the char and the carbonization products must exceed the value of the lignite plus the carbonization costs. From the standpoint of reducing fuel costs for generating electrical energy from solid fuels, such a possibility is of very great interest. Further, the effect of such a development on both the chemical and liquid fuel industries could be important. For the former it would furnish an immense raw-material reservoir of aromatic, alkylated aromatic, and cyclic compounds and for the latter a small but welcome increase in domestic supplies of raw materials for special types of high-energy hydrocarbon fuels.

With the limited available staff and facilities, it was necessary that the low-temperature carbonization work at this station be directed chiefly toward solving problems closely associated with the design and operation of plants; as a result, emphasis was placed on pilot-plant studies (15, 16, 20, 22). A schematic representation of a pilot-plant arrangement is shown in figure 1.

The first work in the tar program at Denver had to do with development of low-temperature-carbonization assay methods (24), and early publications reported the results of laboratory assays on a number of western and European lignites and western subbituminous and bituminous coals. In the procedures developed excellent precision and material balances were reported. Generally, development of methods for testing and analyzing the tars has involved modification and incorporation into composite procedures of methods based upon earlier commercial and Bureau experiences in the analysis of high-temperature tars.

Comparison of Assay and Pilot-Plant Operations

In comparisons between laboratory assays and pilot-plant operations at about 900° F. (482° C.) it was shown (25) that the yield of tar from the latter equals or slightly exceeds that predicted from a laboratory assay at 500° C. and that the yield of gas, char, and water is approximately the same. The temperature of maximum tar formation is about 900° F. (482° C.). Tars produced in a fluidized bed at this temperature are "primary" products, characterized by a high content of higher molecular weight components, pitch, and particularly by high yields of higher boiling phenols.

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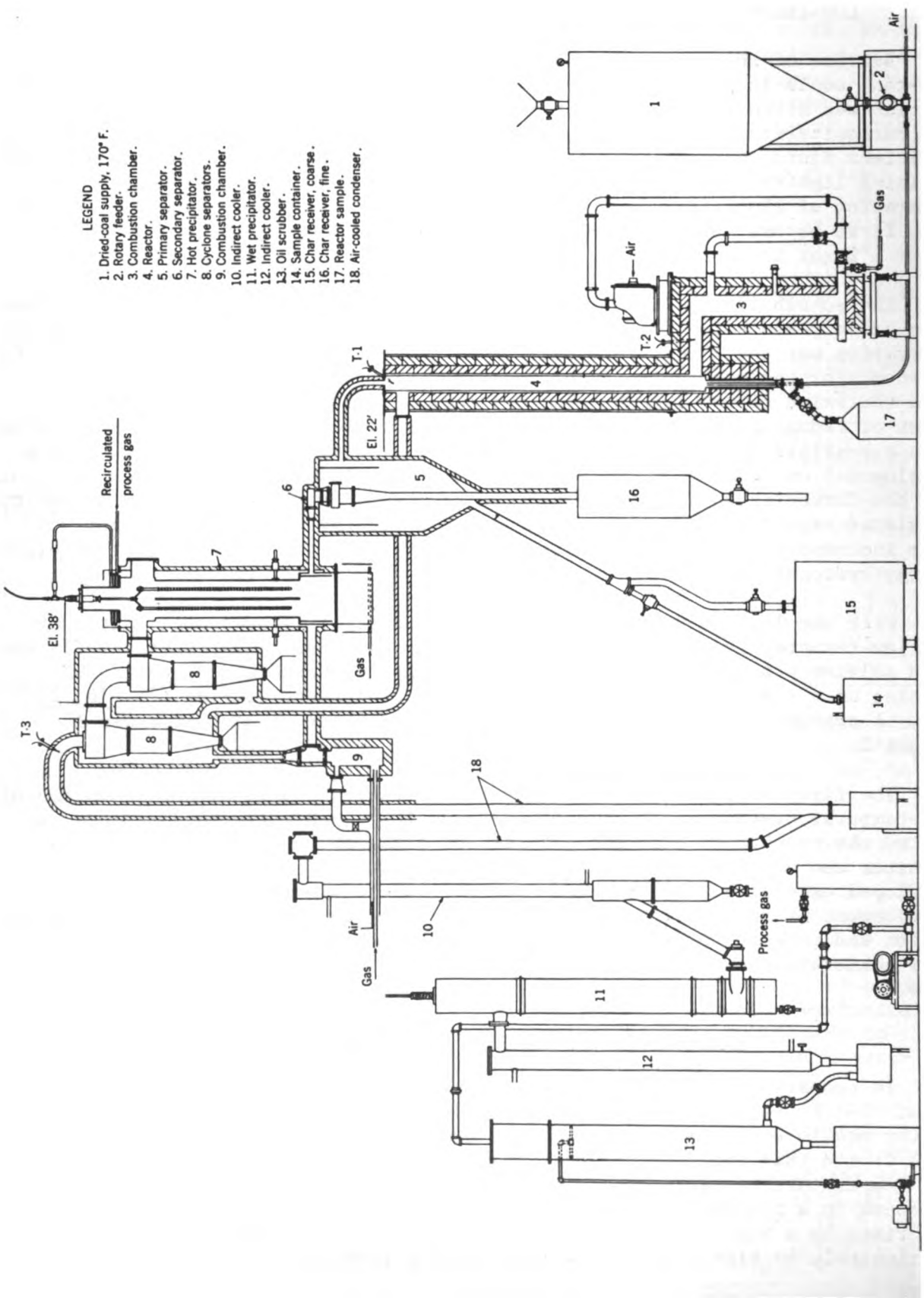

FIGURE 1. - Pilot Plant for Carbonizing Fine Coal, Denver, Colo.; 8-Inch Reactor With Hot Precipitator.

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Effect of Transport Air

In fluid systems where the transport air is allowed to react with the coal to supply both the internal heat required for carbonization and the gases to transport the coal, the yield of tar decreases and the composition changes (25, 26, 44).

This effect is shown by the data in table 2. With the maximum amount of transport air used (2.92 cubic feet of air per pound of moisture- and ash-free coal), the total yield of tar plus light oil is reduced to approximately 66 percent of that in runs where no air was used. The yield of pitch is least affected - it is reduced to 83 percent - and the aromatics, olefines, tar acids, and saturates are reduced to 70, 57, 55, and 50 percent, respectively. The destruction of tar acids and olefins is to be expected, and the considerable reduction in saturates indicates that these are largely naphthenic types.

TABLE 2. - Effect of partial internal heating with air on yield and composition of lignite tar, 900° F. (482° C.).

Yield1/ of tar plus light oil, weight-percent	Specific gravity of tar, 20°/20°	Transport air2/	Tar composition, volume-percent					
			Acids	Bases	Olefines	Aromatic	Saturates	Pitch and loss
11.4	1.042	0.00	19.9	1.2	13.6	11.9	20.7	32.7
11.7	1.045	.00	17.1	2.5	15.4	12.1	19.3	33.6
12.2	1.029	.90	18.4	3.6	15.0	18.9	10.9	33.2
10.2	1.035	2.37	16.7	2.2	14.7	14.4	15.9	36.1
9.8	1.044	2.56	14.9	2.4	16.0	17.6	12.2	36.9
8.9	1.032	2.59	14.0	1.9	15.5	14.0	10.6	44.0
7.6	1.044	2.92	15.6	1.7	12.6	12.8	15.1	42.2

1/ Moisture- and ash-free (m.a.f.) basis.
2/ Cubic feet per pound m.a.f. coal.

Effect of Storage

Changes that may occur in low-temperature tars on aging are important but are not clearly understood. Superficially these changes are indicated by darkening and increased viscosity. They may occur to some extent at normal temperatures and in the absence of oxygen and light, but they are certainly accelerated by increased temperature and/or oxygen and light. The principal effect of aging, however induced, appears to be that of molecular growth, as evidenced by the higher yields of pitch on distillation. Aging studies were made (27) in the Denver laboratories under three conditions:

1. Storage at normal temperatures with restricted access of light and air.

2. Reflux at 125° C. with free access of air to the top of the condenser.

3. Aeration at 80° to 90° C. by bubbling air through the sample.

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The effects of these aging procedures on the distribution of types of components and the boiling ranges are shown in figures 2, 3, and 4.

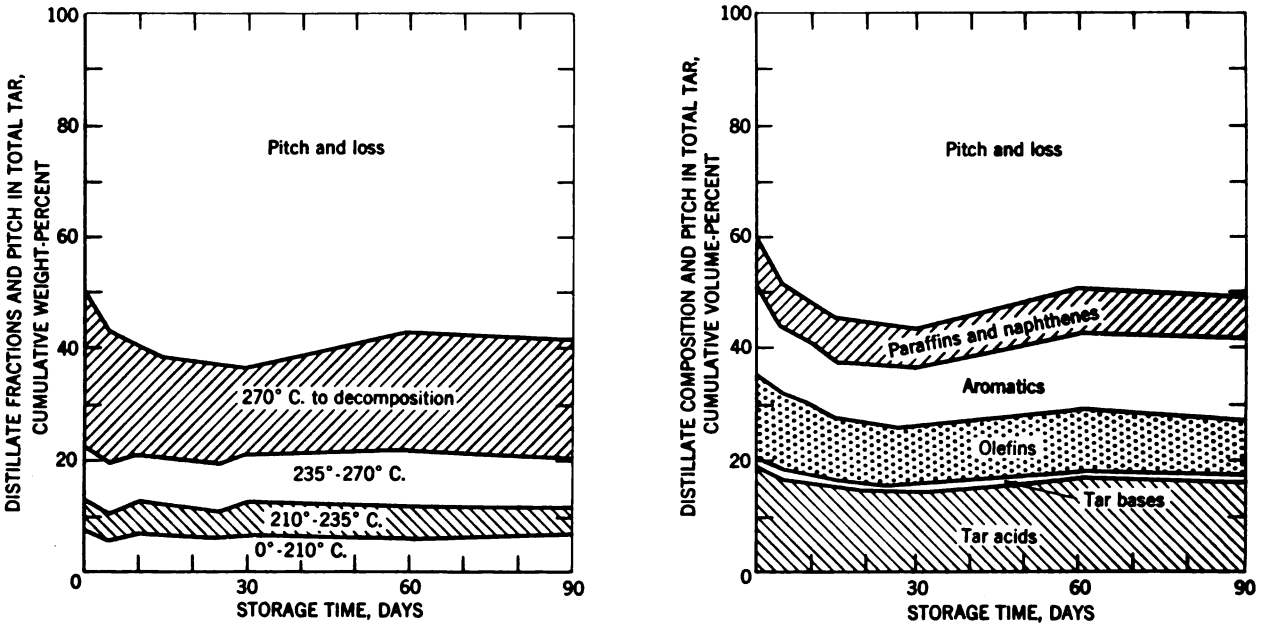

FIGURE 2. - Effect of Storage at Normal Temperatures With Restricted Access of Light and Air on Properties of Sandow Tar.

As would be expected, aging at room temperature with restricted access of air and light resulted in the smallest change in the tar. Even under these conditions, however, there is evidence of molecular growth; pitch fractions increased at the expense of the material boiling above 270° C. Reflux at 125° C. with access of air resulted in a marked increase in pitch content, particularly in the first 12 hours, and decreases in saturates, aromatics, and olefines. An increase in tar acids is shown. Again the increase in pitch was accompanied by a corresponding decrease in the fraction boiling above 270° C. Aeration at 80° to 90° C. resulted in a nearly uniform rate of increase in pitch content for the first 40 days and little change in saturates and significant changes in the aromatic, olefinic, and acidic components. As before, the materials boiling above 270° C. were chiefly responsible for pitch formation.

Effect of Preoxidation

The low-rank coals of the Western United States are high in moisture, and generally reactive, and consequently easily oxidized. Because in fluidized and entrained drying and carbonization processes they may be subjected to oxidizing conditions when air is used as the entraining fluid, it is important to know the effect of oxidation of the raw coal on the yield and composition of the tars. Accordingly, studies (28) were made of the effect of oxidation on the yields of carbonization products of a typical Texas lignite (Sandow).

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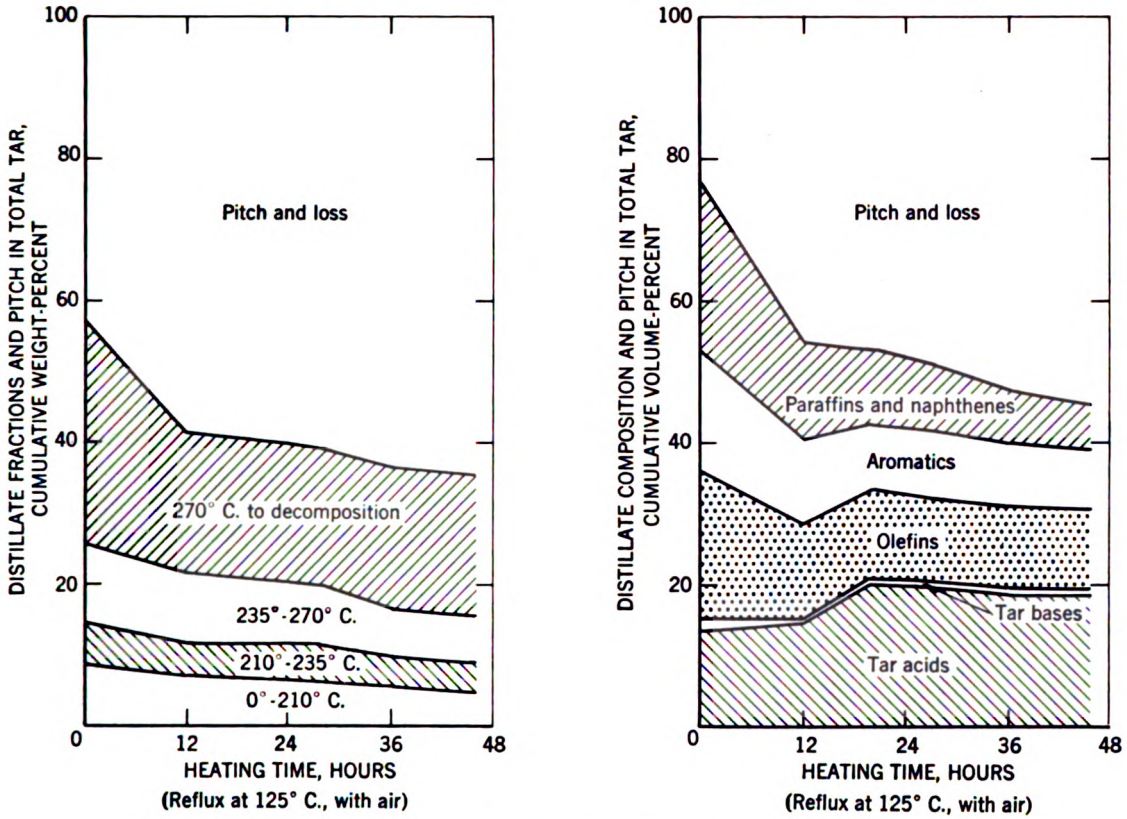

FIGURE 3. - Effect of Reflux at 125° C. With Free Access of Air to Top of Condenser on Properties of Sandow Tar.

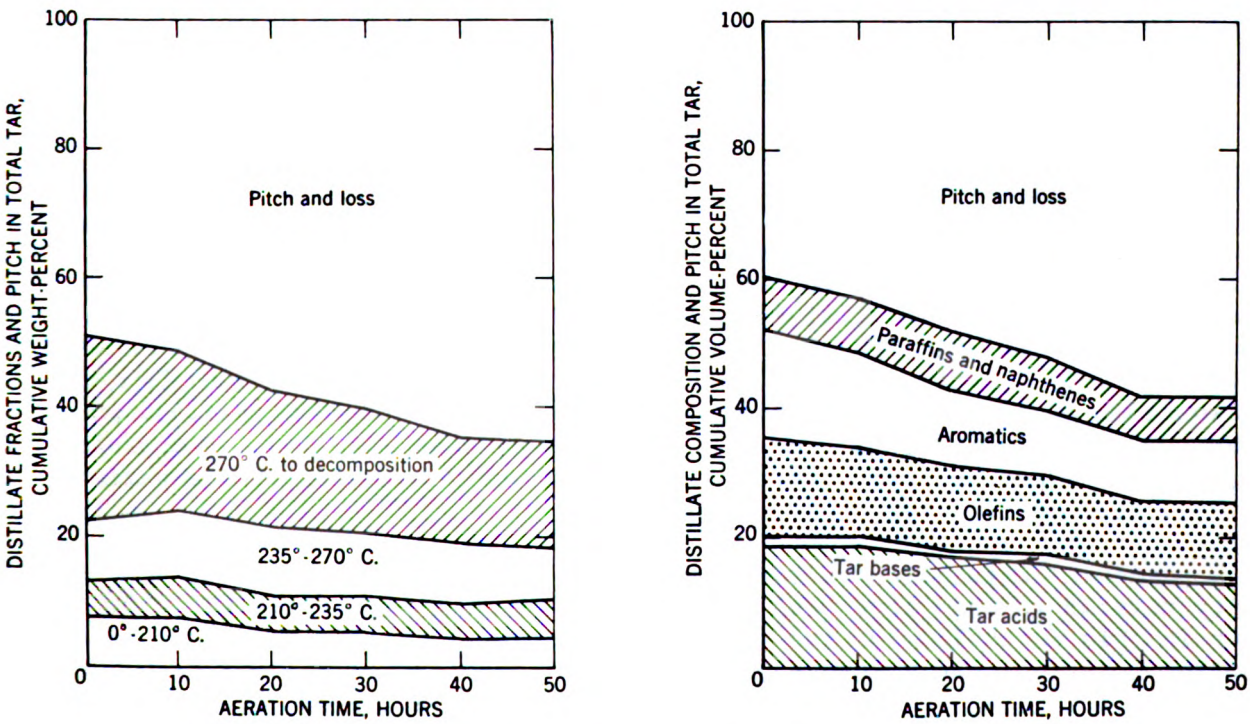

FIGURE 4. - Effect of Aeration at 80°–90° C. by Bubbling Air on Properties of Delcarbon Tar.

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For this purpose three types of treatment were used:

1. Storage in a "slacking oven" at 80° F. (26.6° C.) for 2 to 14 days.

2. Drying in an oven at 105° to 110° C. for 2 to 30 days.

3. Heating in a "muffle type" furnace at 150°, 200°, 250°, and 300° C. for 14 hours.

To determine tar yields, the samples so treated were carbonized at 500° C. in the assay retort.

Even 2 days in the slacking oven resulted in a significant decrease in the yield of tar plus light oil; on the m.a.f. basis raw lignite yielded 16.1 percent, after 2 days this decreased to 14.5 percent, and after 14 to 13.7 percent. As was expected, the rate of decrease in tar yield is greatly accelerated at higher temperatures; 2 days in the drying oven at 105° to 110° C. decreased tar yields to 12.1 percent, and 30 days, to 8.7 percent. The latter figure is only 54 percent of the yield from raw lignite. Treatment at 150° C. for 14 hours resulted in yields of tar plus light oil of 45.3 percent of those from raw lignite. Treatments at 200°, 250°, and 300° C. gave no further significant reductions in tar yields.

Samples alternately wetted and dried at 105° to 110° C. for a total drying period of about 8 days gave yields of tar plus light oil at 53 percent of those from raw lignite. This is of the same order as the yield obtained from samples dried continuously at 105° to 110° C. for 30 days.

Effect of Nature of Coal

Extensive carbonization studies were made (29) on a variety of coals. In this work five lignites, four subbituminous C coals, two subbituminous B, three subbituminous A, and one high-volatile C bituminous coal, and five high-volatile B bituminous coals were carbonized in bench-assay equipment (static bed) and in a pilot plant (entrained in air). The bench assays, with one exception, were made at 500° C. (932° F.). The pilot-plant carbonizations were made at 900° F. (482° C.) to 1,010° F. (543° C.), most of them around 900° F. (482° C.). Mass flows of solids in the pilot plant were varied from 600 to 1,632 pounds per hour per square foot; the greater number of runs were made at approximately 1,100 pounds per hr. per square foot. The amount of transport air varied from 0.0 to 3.76 cu. ft. per pound of solids.

General correlations between yields of tar plus light oil and some quantity related to rank have been reported by a number of workers (15, 30, 31), but in this investigation the yields of tar plus light oil were found to differ greatly, even among coals formally classified in the same rank. This applied particularly to the lignites. Processing variables, over the range studied in the pilot plant, had little effect on the yields of tar plus light oil, and usually bench-assay and pilot-plant yields agreed satisfactorily. There was some evidence of oxidation at long residence times and large ratios

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of transport air, but generally differences in yields of tars plus light oils as well as tar acids appear to depend on specific properties of the coal. Estimated yields of tar products per ton of m.a.f. coal are summarized in table 3. The yield of tar plus light oil from Dakota Star lignite was only 55 percent of that from the Texas Malakoff lignite, but the former furnished 75 percent more tar acids per ton. Such differences undoubtedly reflect the nature of the original vegetable debris in the coalbed.

A linear relation has been found (32) between heat of combustion of volatile matter in coal and tar yield from a laboratory assay at 500° C. (932° F.) (See fig. 5.) This relation permits predictions as to yields of tar plus light oil from routinely determined analytical quantities, since the heat of combustion of the volatile matter is readily calculated from the following relation:

$$H_V = H_C - 0.01 \text{ F. C.} \times 14{,}500,$$

where H_V is the heat of combustion of the volatile matter, in B.t.u. per pound;

H_C is the heat of combustion of the coal, in B.t.u. per pound; and

F. C. is percent fixed carbon - all on the m.a.f. basis.

The effect of temperature in fluid-bed carbonizations on the composition of tars has been studied (29) for Texas Sandow lignite. The temperature range was 900° (482° C.) to 1,100° F. (593° C.); the results are shown in figure 6. With increased temperature of carbonization the pitch content of the tar rose significantly, and the amount of material boiling above 270° C. decreased correspondingly. The increase in pitch resulted primarily from a decrease in aromatic and olefinic components.

Work at this station will continue to be concentrated on engineering and pilot-plant studies. Such studies will be made on samples of Western United States coals obtained by the Bureau and submitted by industry. Correlations will be made of Denver pilot-plant data with corresponding data from industry. Information from various sources on the properties of tars will be collected and compiled. Cooperative studies with industry will be made on the utilization of tar products, and for this purpose special samples and fractions will be prepared. The effects of preoxidation of coals on carbonization will be studied in bench-scale fluid-bed equipment. Bench-scale, low-temperature carbonization assays will continue as required.

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TABLE 3. - Estimated yields of tar products from fluidized-bed carbonization

(All values per ton of m.a.f. coal)

Rank	Lignite					Subbituminous C				Subbituminous B	
Name of coal carbonized	Malakoff	South Arcot	Sandow	Dakota Star	Garrison	Suntrana	Pikeview	Wyodak	Batan	Canari	Elkol
State	Texas	India	Texas	North Dakota	North Dakota	Alaska	Colorado	Wyoming	Philippine Islands	Ecuador	Wyoming
Tar plus light oil....gallons	36.4	22.5	28.3	20.2	14.2	30.3	21.3	32.0	31.4	14.4	39.4
Tar bases ..... pounds	4.0	2.0	3.2	2.3	.7	1.9	3.5	1.9	6.9	1.3	2.4
Tar acids, total ..... do.	41.1	20.1	32.4	73.5	29.8	49.0	27.1	52.5	69.1	21.9	68.3
Phenol ..... do.	2.4	1.5	1.9	1.4	1.0	2.1	1.4	2.2	2.3	1.0	2.9
Cresols ..... do.	6.3	3.9	5.0	3.8	2.6	5.5	3.7	5.8	6.0	2.6	7.6
Xylenols ..... do.	2.4	1.5	1.9	1.4	1.0	2.1	1.4	2.2	2.3	1.0	2.9
Neutral oil, total....gallons	10.5	6.0	12.0	4.8	3.7	7.3	6.8	9.5	4.7	3.5	10.2
Olefins ..... do.	4.8	3.4	5.3	1.2	1.3	4.5	2.6	4.6	1.7	1.4	4.2
Aromatics ..... do.	3.4	1.6	3.7	3.0	1.5	1.5	2.5	2.4	1.9	.9	2.8
Paraffins[1/] ..... do.	2.3	1.0	3.0	.5	.9	1.3	1.7	2.5	1.1	1.2	3.2
Hard pitch ..... pounds	164.0	103.9	97.6	51.9	57.4	135.1	88.9	139.6	158.7	59.7	185.6

Rank	Subbituminous A			High-volatile C bituminous	High-volatile B bituminous				
Name of coal carbonized	Canon Chief	Danao	Osage	Mantalongon	Colombia	Kebler	Spring Canyon	Delcarbon	Kenilworth
State	Colorado	Philippine Islands	Colorado	Philippine Islands	Mexico	Colorado	Utah	Colorado	Utah
Tar plus light oil....gallons	29.2	31.5	28.9	37.6	74.0	33.9	39.1	31.2	45.3
Tar bases ..... pounds	2.0	3.6	4.0	4.0	6.4	3.6	1.3	2.0	4.8
Tar acids, total ..... do.	37.6	59.5	67.4	60.4	50.8	37.6	22.8	29.8	47.3
Phenol ..... do.	2.0	2.3	2.1	2.6	5.0	2.3	2.7	2.4	3.3
Cresols ..... do.	5.3	5.9	5.5	6.8	13.1	5.9	7.0	6.2	8.7
Xylenols ..... do.	2.0	2.3	2.1	2.6	5.0	2.3	2.7	2.4	3.3
Neutral oil, total....gallons	9.2	7.7	9.0	13.6	22.8	10.2	9.2	19.1	13.8
Olefins ..... do.	3.0	3.0	3.0	4.1	7.5	3.8	6.4	6.6	5.2
Aromatics ..... do.	2.9	2.2	3.8	4.2	8.5	2.8	1.3	5.2	4.8
Paraffins[1/] ..... do.	3.3	2.5	2.2	5.3	6.8	3.6	1.5	7.3	3.8
Hard pitch ..... pounds	132.3	152.4	108.9	152.5	381.8	140.5	225.0	107.7	236.2

1/ Paraffin fraction includes naphthenes.

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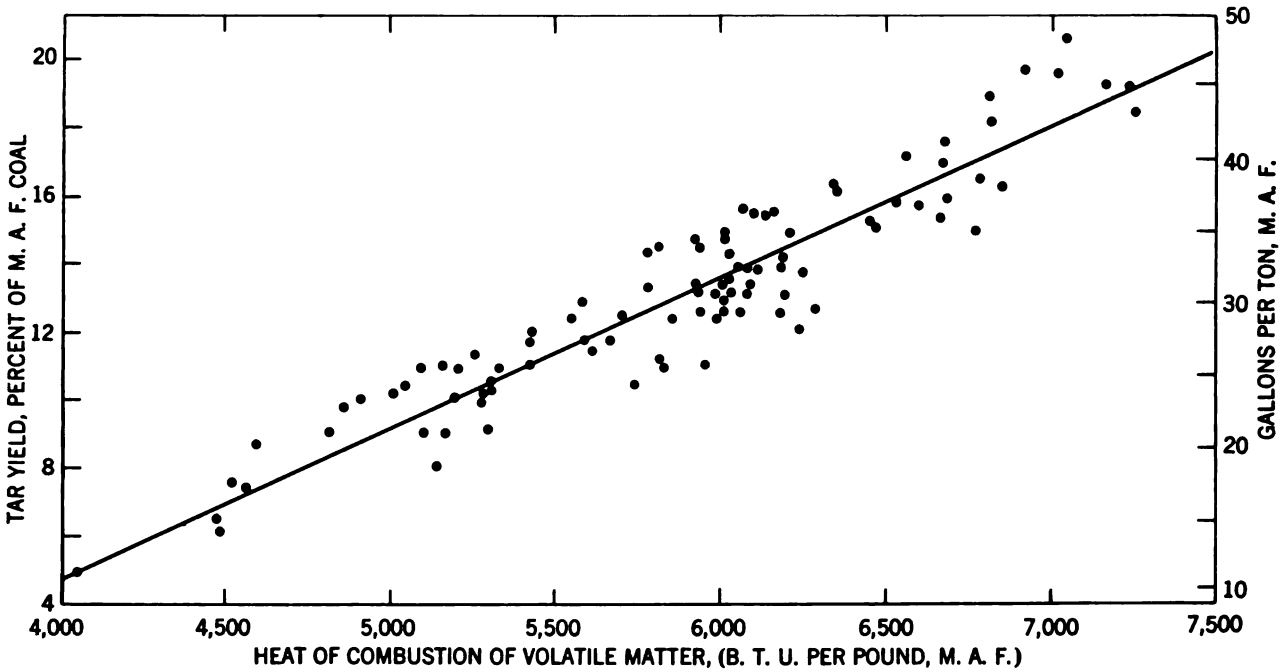

FIGURE 5. - Relation Between Yield of Tar and Heat of Combustion of Volatile Matter.

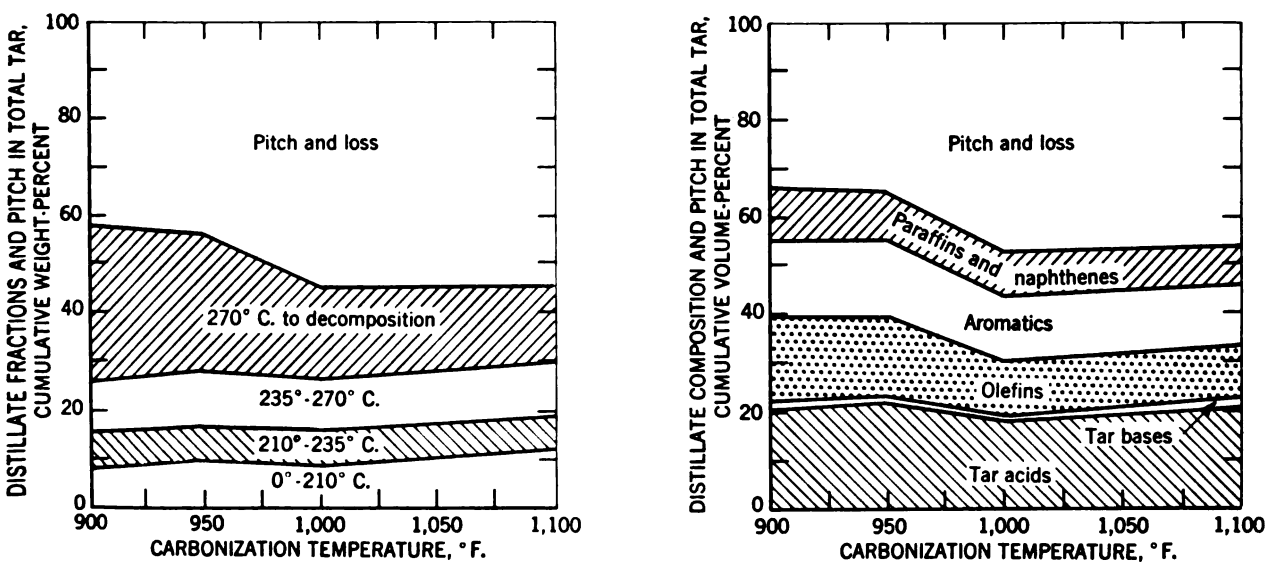

FIGURE 6. - Effect of Carbonization Temperature on Composition of Sandow Tar Distillate.

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INVESTIGATIONS AT LIGNITE EXPERIMENT STATION, GRAND FORKS, N. DAK.

General Program

The work at Grand Forks has been in two fields: (1) A broad study of the carbonization characteristics of North Central lignites as determined by laboratory assays and (2) a detailed characterization of the tars produced by a commercial low-temperature carbonization plant at Dickinson, N. Dak.

In carrying out the first phase of the work, face or column samples were obtained from 23 operating mines in western North Dakota and 8 core-hole samples from contiguous regions of South Dakota and Montana; the latter resulted from drilling operations of the Great Northern Railroad.

Samples were carbonized (33) in bench-scale assay equipment similar to that developed at Denver (24).

Most assays were run to a maximum temperature of 500° C., considered to be optimum for yield of tar and light oil. A few runs to 450° and 550° C. demonstrated the minor differences resulting at these temperature levels. The data show general uniformity; the yield of tar plus light oil averaged 8 percent on a m.a.f. basis but ranged from 3.3 percent for a fusain (fusinite) concentrate to as high as 11 percent for a normal sample.

With few exceptions, there was little evidence of any effect of geographical location on product yields; often samples from two mines in the same bed showed as much variation as samples from mines in different beds.

Data on undried samples and those dried in saturated steam at 598° F. (314° C.) and 1,500 p.s.i.g. showed surprisingly little difference in view of the marked changes in superficial appearance and structure. On a m.a.f. basis yields of char increased; tar yields were unchanged; total gas yields decreased, owing to loss of carbon dioxide; and illuminants and carbon monoxide in the gas increased. There was also a small but significant decrease in hydrogen sulfide. These changes must have resulted from volatilization of components, other than water, that were not lost in normal drying. The large loss of carbon dioxide, with the increase in char yields and no increase in tar and light oil, is characteristic of humic acid types of compounds where the carboxyl groups lost have been attached to highly condensed nuclear structures. The gases liberated during steam drying amounted to 4.42 weight-percent of the lignite charged and contained 96 percent carbon dioxide.

Carbonization of samples, enriched in the various petrographic components by hand selection, showed that anthraxylon and translucent attritus (essentially vitrinite) gave high tar yields, whereas samples rich in opaque attritus (largely micrinite) and fusain (fusinite) gave higher yields of char. The high carbon dioxide content of gaseous products was also characteristic of the last two.

The effect of partial oxidation of the sample before carbonization was clearly demonstrated. Yields of char plus light oil were lower, and yields of

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gas, higher from samples from slack seams (weathered) or from the highly oxidized "leonardite." The gaseous products from the carbonization of oxidized samples were notably higher in carbon dioxide.

Study of a Commerical Tar

A low-temperature carbonization plant has been operating intermittently at Dickinson, N. Dak., since 1928. This plant carbonizes North Dakota lignite in an internally heated retort, based upon German design, and is now being operated part time by the Dakota Briquetting Co. The capacity is 100 to 150 tons per day of as-mined lignite, and the yield of tar is about 5 gallons per ton. This corresponds to approximately 70 percent of the laboratory-assay yield. The tars and oils, after separation from the water condensate, are roughly fractioned by distillation into liquids and pitch. This liquid distillate is marketed as a wood preservative and is the primary material used in tar investigations by this station since 1954.

This tar fraction, which boils to 350° C. and represents about 50 percent of the total tar, is composed of approximately equal parts of alkali-soluble compounds (tar acids) and a highly aromatic neutral oil; a small percentage of bases is also present.

The methods of separation and characterization are outlined in figure 7.

Samples were distilled in random-pack or Heli-Grid columns at various pressures, generally under inert atmospheres; acids and bases were separated by conventional methods and by countercurrent extraction with an aqueous methanol-hexane combination in a column of the York-Scheibel type. A spinning-band distillation column was used in precise fractionation of both experimental and synthetic material.

Preliminary work with thermal diffusion indicates that this method effects some concentration of components of wide-boiling fractions of tar acids but it has not been successful in separating individual compounds.

Gas-liquid partition chromatography readily separates the lower boiling tar acids and, after extensive experimentation with stationary liquid phases, is being used with success on higher boiling materials. Apiezon L stopcock grease supported on crushed firebrick has proved the most satisfactory separating medium for the phenolic compounds. At present, emphasis is on separation and identification of components of narrow boiling tar-acid fractions. Their properties, composition as so far determined, as well as recoveries are shown in table 4. Of special interest have been the isolation and identification of derivatives of orthodihydroxy benzenes, the catechols. These are generally more valuable and rarer than monohydroxy benzenes.

A catalog was needed of infrared spectra of aromatic hydroxy compounds for comparison with spectra of tar constituents isolated by distillation or chromatographic techniques. By purchase and purification or synthesis in this laboratory, over 100 compounds have been obtained and their spectra recorded from 2 through 15 microns. These spectra are now being processed for publication by the Bureau of Mines. New chromatographic separation techniques,

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followed by identification by infrared spectra, have made possible the qualitative and quantitative picture presented in table 4.

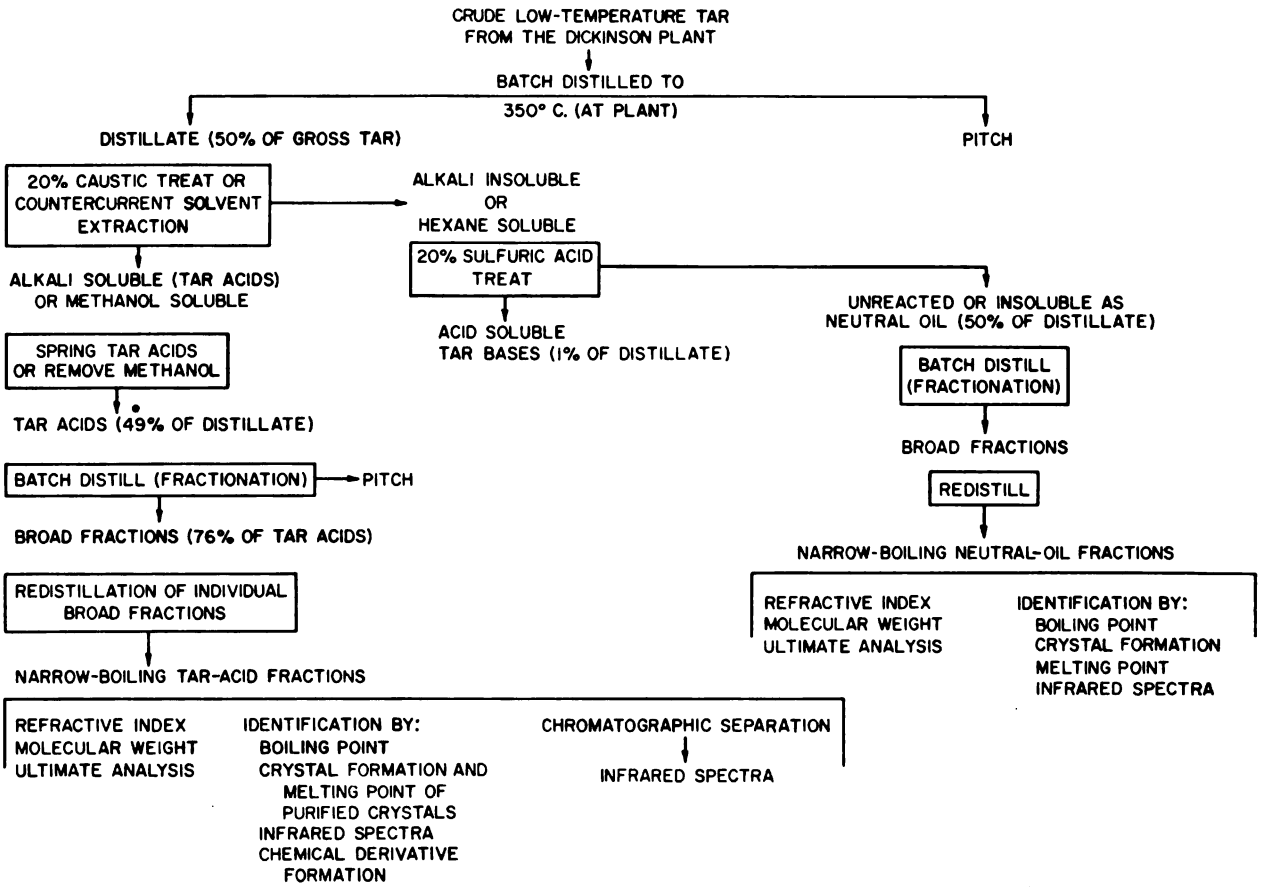

FIGURE 7. - Summary of Characterization of Lignite Tar by the Lignite Experiment Station, Grand Forks, N. D.

Narrow-boiling fractions of the highly aromatic neutral oil ranged in molecular weight from 140 to 350, had H/C atomic ratios of 1.35:1.68, and had indices of refraction n_D^{20} of 1.4524 through 1.5408. Naphthalene, methyl naphthalene, and anthracene as well as paraffinic material, have been isolated and characterized in the range of 20 to 24 carbon atoms per molecule. Investigation of this material, largely by displacement or elution chromatography on silica gel, showed a high degree of unsaturation as well as of aromaticity.

The higher boiling neutral materials all contain oxygen, nitrogen, and sulfur in significant amounts, indicating a great variety of heterocyclic compounds.

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TABLE 4. - Properties and composition of tar-acid fractions

General properties

Molecular weight ..... 124-197.
Atomic H/C ..... 1.125-1.343.
Methoxyl ..... percent 0.38-4.91.
Index of refraction n_D^{20} ..... 1.5079-1.6057.

Components identified	Tar acids, percent	Distillate, percent	Crude tar, percent
Phenol	5.9	2.9	1.5
o-Cresol	2.8	1.4	.7
m-Cresol	4.7	2.4	1.2
p-Cresol	4.7	2.4	1.2
2,3-Xylenol	.6	.3	.2
2,4-Xylenol	1.4	.7	.4
2,5-Xylenol	1.2	.6	.3
2,6-Xylenol	.2	.1	-
3,4-Xylenol	1.5	.8	.4
3,5-Xylenol	.7	.4	.2
o-Ethyl phenol	.3	.2	.1
m-Ethyl phenol	.3	.2	.1
p-Ethyl phenol	1.6	.8	.4
Guaiacol	1.3	.7	.4
4-Methylguaiacol	3.2	1.6	.8
4-Ethylguaiacol	1.4	.7	.4
Pyrocatechol	2.6	1.3	.7
3-Methylpyrocatechol	.8	.4	.2
4-Methylpyrocatechol	1.1	.6	.3
3,6-Dimethylpyrocatechol	.1	-	-
3-Ethylpyrocatechol	.2	.1	-
4-n-Propylpyrocatechol	-	-	-
b-Naphthol	1.6	.8	.4
5-Methyl-b-Naphthol	-	-	-

WORK AT APPALACHIAN EXPERIMENT STATION, MORGANTOWN, W. VA.

In December 1954 Congress was requested to provide funds for a much-expanded program of research on low-temperature tars. The purpose of this program was "... to develop through analysis and research end uses and realization values for low-temperature tars and products therefrom...."

Uses for low-temperature tar have not been developed, because the raw material has not been available. It is a distinctly different material from high-temperature tar and does not fit into the end uses of coke-oven (high-temperature) tars. However, low-temperature carbonization will yield chars highly suitable for power plant use as well as substantially larger amounts of tars and liquid products than high-temperature carbonization. With development of end uses to yield proper credit values for the low-temperature tars, coal could be much more efficiently used to provide minimum cost power and a valuable, expanded organic chemical industry.

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In the spring of 1955, when it appeared probable that the Congress would act favorably on the Bureau request, a planning conference was arranged between Bureau personnel and representatives of industry. At this meeting, held in Pittsburgh on April 22, 1955, the program was divided into three main categories:

1. Separation and characterization of commercial and experimental tars.

2. Upgrading of whole tar and selected tar fractions.

3. Utilization: Preparation of fractions for commercial evaluation.

It was the consensus of the industrial representatives that in the early phases of the program the Bureau should concentrate on characterizing tar fractions according to types, with special emphasis on those fractions boiling above 300° C. The importance of category 1 was further stressed by an industrial representative, who pointed out that the Bureau should go much farther into separation and identification than industry.

Funds were made available for the Morgantown tar program on July 1, 1955. At the end of the first year of operations, June 30, 1956, three laboratories had been equipped; these were occupied on May 25, 1956.

When this report was written the facilities consisted of five laboratories; each was equipped for a specific function:

1. Chromatography and extraction.

2. Distillation and synthesis.

3. Secondary chemical reactions.

4. Instrumental analysis.

5. Determination of physical properties.

Because the station had no facilities for high-pressure experiments, a suitable area was prepared.

Methods of Characterization

The major methods adopted at Morgantown for separating and characterizing low-temperature tars and derived products are distillation, solvent extraction, and chromatography. Some of the laboratory equipment is shown in figures 8, 9, and 10.

Identifications have depended on infrared and ultraviolet spectrophotometry and determination of physical properties. Since not enough spectra of simple alkyl phenols were available for comparison with even the lowest boiling tar acids, a number of these, as well as some polycyclic phenols, have been synthesized; likewise, some polymethylquinolines had to be synthesized

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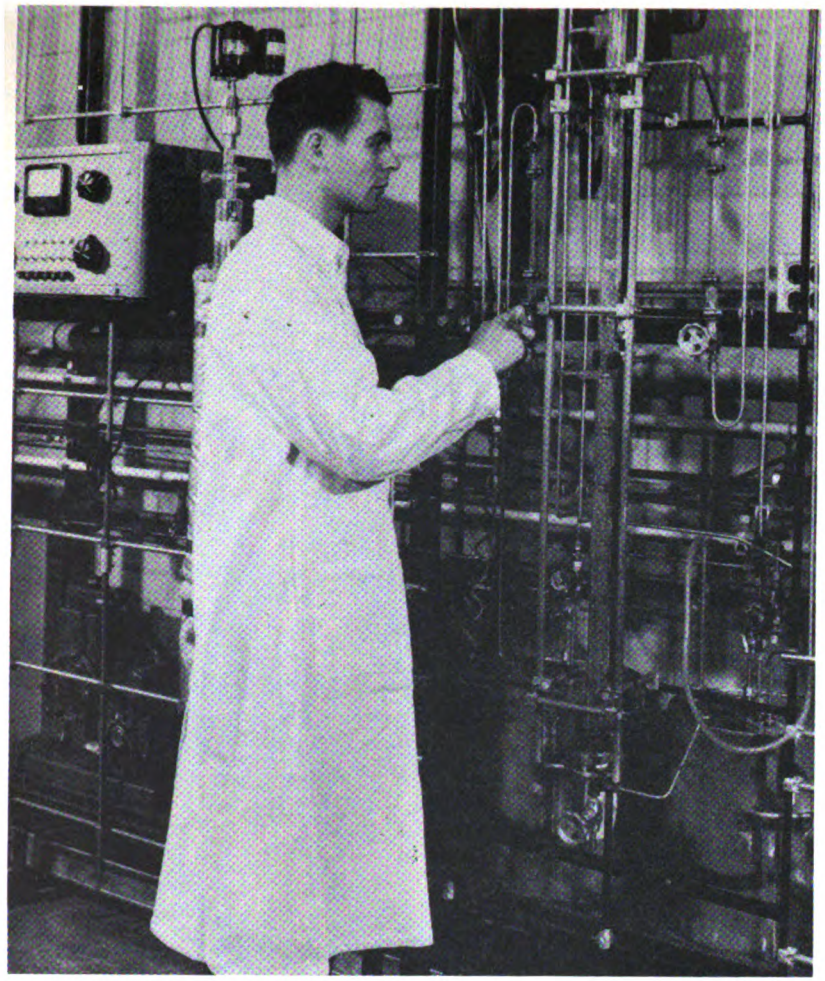

FIGURE 8. - Operation of Packed Column for Solvent Fractionation.

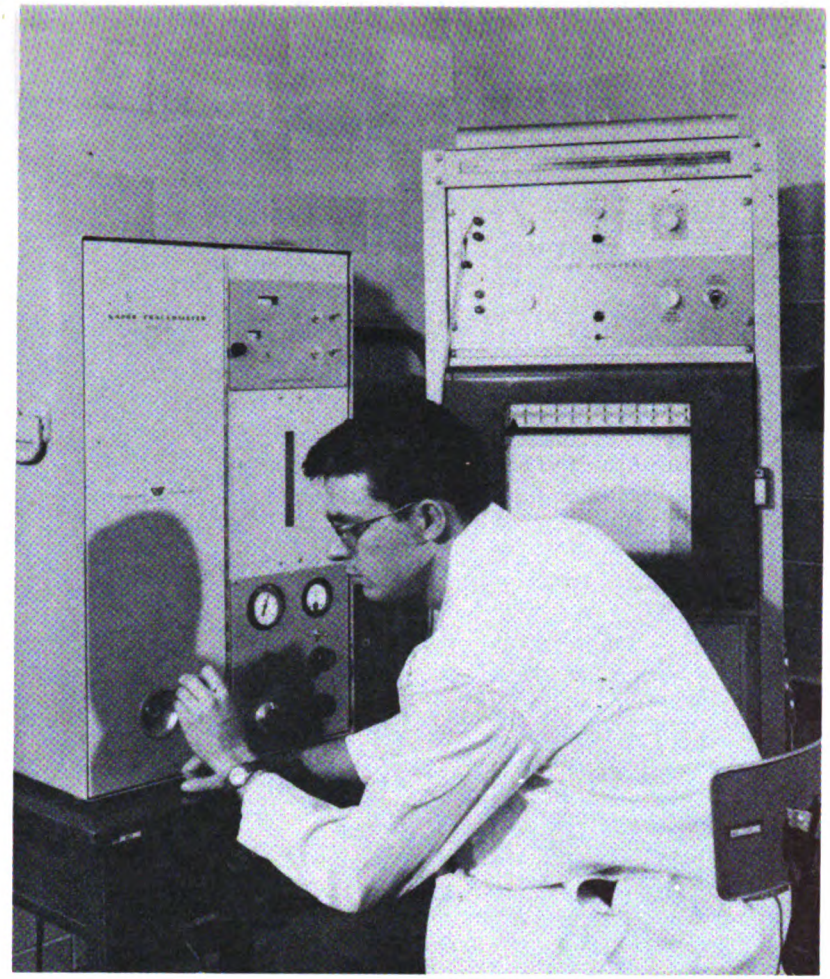

FIGURE 9. - Gas-Liquid-Partition Chromatography Apparatus.

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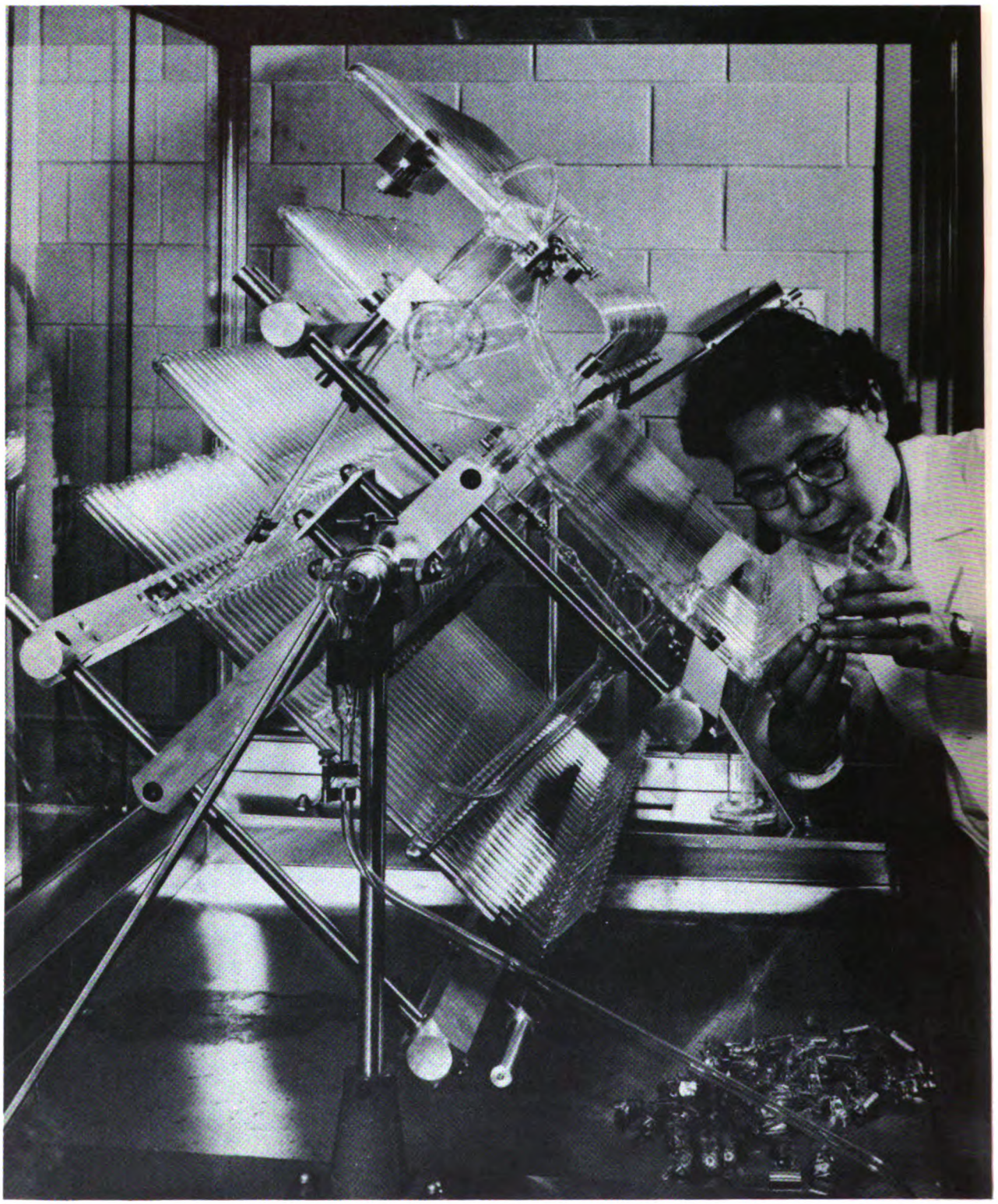

FIGURE 10. - Countercurrent Distribution Instrument for Fractionating Phenolic Compounds in Coal Tars.

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Because they comprise about 35 weight-percent of the total tar bases (34). As no listing of phenols and their physical properties existed that included enough compounds to be practicable, a compilation of the physical properties of 183 low-boiling phenols was made and published (35).

Special types of titration have also been used (36). The general separation program for low-temperature coal tar and pertinent laboratory and instrumental facilities have been described (37).

Characterization of Tar Acids, Tar Bases, and Neutral Oils

A method of applying vapor-phase chromatography to tar acids has been developed (38, 39). Quantitative determinations by the independent methods of infrared spectrophotometry and vapor-phase chromatography have been made of the tar acids boiling to 234° C. Eighteen phenolic components have been identified (40). (See table 5.) The presence of nine major higher boiling phenols has been established by countercurrent distribution: 3,4,5-trimethylphenol, 4-indanol, 5-indanol, 1-naphthol, 4-methyl-1-naphthol, 2-naphthol, 2-phenylphenol, 3-phenylphenol, and 4-phenylphenol.

An ultraviolet spectrophotometric method for determining total pyridines and total quinolines in coal distillates has been developed and described (41).

TABLE 5. - Comparison of infrared (IR) and gas-liquid partition chromatographic (GLPC) analysis of phenols

Compound	Weight-percent in total tar acids		
	IR		GLPC
Phenol	1.4		1.9
o-Cresol	3.2		5.1
m-Cresol	8.7	14.6	11.8
p-Cresol	5.9		
2,4-Xylenol	9.7	13.6	12.8
2,5-Xylenol	3.9		
2,6-Xylenol	1.0		1.3
o-Ethylphenol	(1/)		1.5
m-Ethylphenol	2.5	12.2	10.9
p-Ethylphenol	2.5		
2-n-Propylphenol	(1/)		
2,3-Xylenol	1.3		
3,5-Xylenol	5.9		
3,4-Xylenol	3.7	8.2	7.9
Unknown	(1/)		
4-Ethyl-2-methylphenol	4.5		
3-Ethyl-5-methylphenol	3.0	7.9	5.4
2,3,5-Trimethylphenol	4.9		
2,4,6-Trimethylphenol	(1/)		1.4

1/ Quantitative infrared analysis impossible.

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By fractional distillation and infrared and ultraviolet spectrophotometry, 51 individual tar bases were identified and their quantities determined (see table 6). In studying the sorption of pyridine bases by cation-exchange resins, an ultraviolet spectrophotometric method was developed, which can be applied to dilute solutions (42).

A procedure has been developed whereby the maximum number of aromatic hydrocarbons in neutral oils can be determined with a minimum of effort and sample. This consists of fractional distillation into narrow boiling cuts, displacement chromatography of these cuts to isolate aromatic fractions, separation of the aromatic fractions into nearly individual compounds by gas-liquid partition chromatography, and collection of gas-chromatographic fractions for micro-infrared analysis. By these means a sample of neutral oil from bituminous coal low-temperature tar has been shown to contain 15 major components: 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1,3-dimethyl-3-ethylbenzene, 1-methylindan, 5-methylindan, 1,2-dimethylindan, indene, 2-methylindene, 3-methylindene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1,2,3,4-tetrahydronaphthalene, and biphenyl.

By elution chromatography the pitch, or distillate residue, has been separated to yield various neutral oil fractions. The acidic and basic compounds are among the most strongly adsorbed fractions. The initial colorless oils and solids have been shown by ring analysis and ultraviolet spectrophotometry to be free of aromatics and to consist of dinuclear naphthenes with a high degree of alkylation. The very viscous yellow-orange oils subsequently obtained have been shown by ring analysis to consist mainly of alkylated anthracenes and phenanthrenes.

Pilot-Plant Fractionations and Secondary Reactions

Several procedures have been considered. They fall into two large groups: (1) Separation techniques and (2) chemical conversions.

Pilot-plant equipment available for this work now includes a tar still and two reactors, two autoclaves, a solvent-extraction column, and a fractional-distillation unit. The first efforts in this field have been directed toward separations of tar acids and neutral oils by procedures adaptable to large-scale operation.

Low-temperature tar contains a large fraction of high-boiling tar acids. Extraction with aqueous caustic soda is not completely effective for their recovery. Monoethanolamine (MEA) has been found useful for this purpose; the yield of phenolic compounds recovered by this reagent is of the same order as that obtained with alcoholic potassium hydroxide. The relations between concentration of MEA, oil-to-solvent ratio, concentration of tar acids in distillate, and yield and purity of the product have been investigated.

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TABLE 6. - Quantitative analysis of low-temperature tar bases

Compound	Weight-percent in total tar bases	Compound	Weight-percent in total tar bases
2,3-Dimethylpridine	0.01	3,4-Dimethylquinoline(?)	0.89 to 1.76
2,4-Dimethylpyridine	.45	4,6-Dimethylquinoline(?)	.84 to 1.8
3,5-Dimethylpyridine	.04	2,4,6-Trimethylquinoline	3.41
2,3,5-Trimethylpyridine	.38 to .78	2,4,7-Trimethylquinoline	2.85
2,4,6-Trimethylpyridine	.87	2,4,8-Trimethylquinoline	2.81
3-Ethyl-4-methylpyridine	.88	2,6,8-Trimethylquinoline	2.25
4-Ethyl-2-methylpyridine	.07 to .15	Acridine (2,3-Benzoquinoline)	.13
5-Ethyl-2-methylpyridine	.48	Phenanthridine (3,4-Benzoquinoline)	.48
4-Isopropylpyridine	.06 to .12	Benzo /f/ quinoline (5,6-Benzoquinoline)	1.3 to 2.96
2,3,4,6-Tetramethylpyridine	.57 to 1.4	Benzo /h/ quinoline (7,8-Benzoquinoline)	1.09 to 2.19
2,3,5,6-Tetramethylpyridine	.16 to .32	2,4-Dimethylbenzo /f/ quinoline (?)	(?)
2,6-Dimethyl-4-ethylpyridine	.3 to .6	2,4-Dimethylbenzo /g/ quinoline (?)	(?)
3,4-Diethylpyridine (?)	.32 to .93	2,4-Dimethylbenzo /h/ quinoline (?)	(?)
2,3-Cyclopentenopyridine	.10 to .22		
2-Phenylpyridine	.47 to 1.58		
4-Phenylpyridine	.72 to 1.7	Aniline	.26
2-Methyl-6-phenylpyridine (?)	.48 to .96	N,N-Dimethylaniline	.06
		N-Methyl-2-methylaniline	.16
Quinoline	1.86	3-Methylaniline	.48
2-Methylquinoline	2.36	2,5-Dimethylaniline	.22
4-Methylquinoline	3.21	2,6-Dimethylaniline	.60
6-Methylquinoline	.44	3,5-Dimethylaniline	.77
7-Methylquinoline	1.02	2-Ethylaniline	.22
8-Methylquinoline	.33	N-Benzyl-2-methylaniline	.19
2,4-Dimethylquinoline	5.92	N-Benzyl-4-methylaniline	.29
2,6-Dimethylquinoline	1.95	2-Naphthylamine	.63
2,7-Dimethylquinoline	.64 to 2.07		
2,8-Dimethylquinoline	1.89	Total	45.9 to 57.1

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Development of methods adaptable to large-scale operations for separating neutral oils according to chemical type is recognized as an important part of the program. Solvent extraction with furfural has been started, following the approach of Hunter and Nash (43). Preliminary results with the system neutral oil-furfural-hexane in a column of 12 theoretical stages have shown some enrichment of aromatic and nonaromatic fractions. Work with more selective solvents, such as oxydipropionitrile $(C_2H_4CN)_2$-O, is underway.

Assay Work on Tar Acids and Bases

For guiding the development of these separation processes, information on the concentration of individual tar acids and tar bases is highly desirable. Although the Denver group has done much general assay work on lignite tars, determination of individual tar acids has not been reported, except for one sample (44). On the basis of a modified infrared spectrophotometric procedure for tar acids (40) and the ultraviolet technique (41) for total pyridines and quinolines, individual tar acids and total pyridines and total quinolines have been identified in a number of tars. The results so obtained, as well as those reported by the Grand Forks station and British workers (45), are shown in tables 7 and 8.

In the four tars from Wyoming coals tar acids boiling above the range of xylenols represent 75 percent of the total in comparison with 25 percent for high-temperature tars.

A tar from Sandow (Texas) lignite has also been assayed. By simple distillation in a batch still the tar was topped to 280° C. at a vacuum of 29 mm. of mercury. Distillate was 54.3 percent by volume, the pitch 39.1, water 2.1, and losses 4.5 percent. The volume composition of the distillate was: Tar acids 31.0 percent, tar bases 3.8 percent, and neutral oils 65.1 percent. A waxy material (m.p. 37° to 46° C.) was isolated from the residue resulting from distillation of the neutral oils in a yield of 1.9 percent of the neutral oil.

Present Program

The plans for characterization research can be visualized from figure 11, which shows accomplishments to date and areas that need more extensive examination. Thus work in the immediate future will deal with characterization of higher boiling tar acids, neutral oil from distillate, and cyclohexane solubles in pitch. Distillable neutral oils constitute approximately 17 percent of the dry tar, and the last fraction about 18 percent.

For the longer range, characterization work will be continued on the cyclohexane-soluble brown semisolid from pitch and on the cyclohexane-insoluble black solids from pitch, which together constitute 61 percent of the tar.

Separations will be made by continuous solvent extraction and/or distillation and adsorption to recover fractions greatly enriched in one type of component, for example, tar acids, tar bases, aromatics, olefins, naphthenes, or paraffins.

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TABLE 7. - Assay of tar acids in tars from certain western coals and in a British tar, in percent

	Wyodak		Big Horn		Hanna		Stansbury		North Dakota lignite		British low-temperature tar	
	Tar acids	Whole tar	Tar acids	Whole tar	Tar acids	Whole tar	Tar acids	Whole tar	Tar acids	Whole tar	Tar acids	Whole tar
Total tar acids ...	100	10.3	100	18.0	100	11.4	100	11.8	100	-	-	29.3
Phenol	6.9	.71	4.0	.7	5.53	.63	3.44	.41	13.9	-	-	1.52
o-Cresol	3.7	.38	2.1	.4	2.98	.34	2.48	.30	6.0	-	-	1.69
m-Cresol	6.2	.65	2.8	.5	3.90	.44	4.0	.47	10.8	-	-	1.55
p-Cresol	6.4	.67	4.4	.8	5.39	.61	4.6	.54	11.3	-	-	1.36
2,3-Xylenol	.13	.013	.2	.05	-	-	.46	.06	1.0	-	-	-
2,4-Xylenol	2.3	.23	2.2	.4	-	-	5.62	.66	1.9	-	-	-
2,5-Xylenol	.9	.09	1.2	.2	1.23	.14	.93	.10	1.8	-	-	7.30
2,6-Xylenol	.1	.01	-	-	.11	.01	.1	.01	.3	-	-	-
3,4-Xylenol	-	-	.9	.2	-	-	.75	.09	2.1	-	-	-
5,5-Xylenol	-	-	1.1	.2	-	-	1.33	.16	.9	-	-	-

TABLE 8. - Assay of tar bases in tars from certain western coals and in a British tar, in percent

	Wyodak		Big Horn		Hanna		Stansbury		Nugget	
	Tar bases	Whole tar	Tar bases	Whole tar	Tar bases	Whole tar	Tar bases	Whole tar	Tar bases	Whole tar
Sum of pyridines and quinolines	100	0.31	100	0.12	100	0.46	100	0.40	100	0.38
Total pyridines	82.0	.25	84.8	.11	81.0	.37	79.5	.32	81.4	.31
Total quinolines	18.0	.06	15.2	.01	19.0	.09	20.5	.08	18.6	.07

	Brillant		D. O. Clark		North Dakota lignite		British low-temperature tar	
	Tar bases	Whole tar	Tar bases	Whole tar	Tar bases	Whole tar	Tar bases	Whole tar
Sum of pyridines and quinolines	100	0.31	100	0.33	-	0.54	-	2.08
Total pyridines	76.0	.24	72.7	.24	-	-	-	-
Total quinolines	24.0	.07	27.3	.09	-	-	-	-

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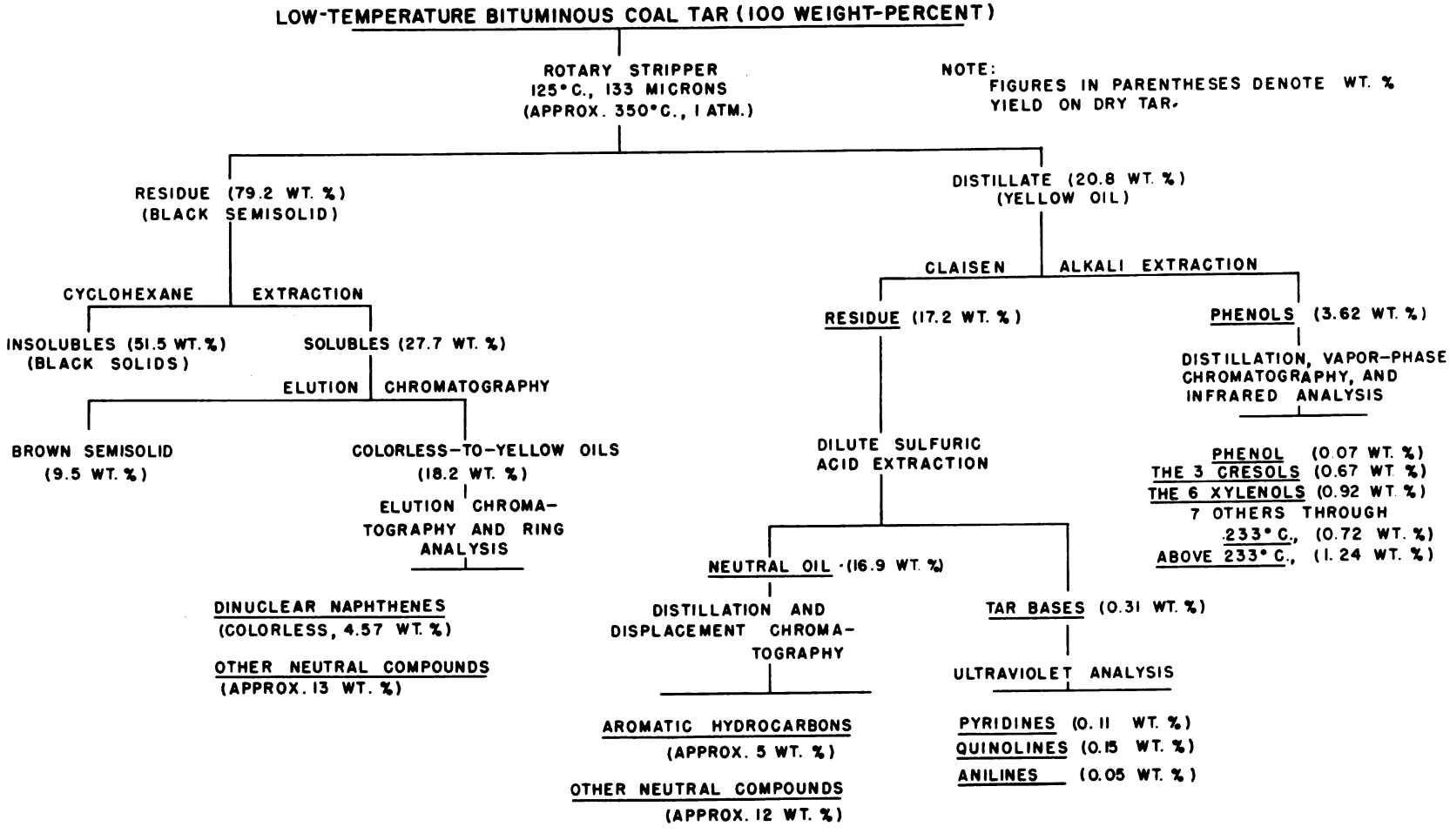

FIGURE 11. - Separation and Characterization Procedures at Morgantown, W. Va.

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Chemical conversions, such as dealkylation of alkylated phenols, formation of aromatics from alkylated aromatics, dehydrogenation of naphthenes, and destructive hydrogenation of higher molecular-weight hydrocarbons will be considered as enriched fractions become available.

UTILIZATION

As was pointed out earlier there will probably be few localities in the Unites States where, in the foreseeable future, any significant premium can be obtained for heat units in the form of low-temperature chars.

Special uses for chars, such as blending in mixes for metallurgical coke, gasification, and chemical utilization may be envisioned, but any premium obtained for such uses generally will be limited to the equivalent transportation costs of coals with suitable properties from nearby areas. Because of local conditions, a unique demand might exist for low-temperature chars, but it is improbable that these locations will be of any considerable magnitude.

Thus utilization of tar will probably be the primary factor controlling the magnitude of any low-temperature carbonization industry in the United States.

To understand this problem one must have some concept of the quantities of such tars that might be available. If all the energy, equivalent to approximately 150 million tons of coal used annually in the United States to generate electricity, were supplied by char from fluid-bed carbonization, approximately 4 billion gallons of low-temperature tar would be available. This figure is based upon a char yield of 75 percent and a tar yield of 20 gallons per ton of coal. For chemical utilization this would be a very large supply, but in terms of crude liquid-fuel resources it amounts to only a few percent of our present annual requirements. Thus, any considerable low-temperature-carbonization industry must look to both fuel and chemical utilization of the tar products. For both fields of utilization, knowledge of the components is of first importance. With present prices for crude petroleum, tar is too expensive to be processed like crude petroleum; furthermore, because of the large content of condensed cyclic structures in the tar, many conventional petroleum-processing methods are ineffective.

Although the exact course followed in low-temperature tar utilization will doubtless depend on geographic location and other specific economic factors, the following path appears probable:

Low-boiling tar acids and tar bases will be separated directly from the tar and will find chemical uses.

The higher boiling tar acids will either be cracked to simpler compounds or used directly as wood preservatives and disinfectants.

The neutral components in the range of two to four rings, after saturation with hydrogen, may be used as special fuels where their high heating value per unit volume is of unique interest.

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The utilization of pitch probably will be confined to mechanical applications as binder and for conversion by carbonization to low-ash carbons. The use of pitch from low-temperature tar as a binding material in electrode manufacture appears to be handicapped by its low aromaticity and high hydroxyl content.

Because of the high pitch content of low-temperature tars, effective utilization constitutes a critical problem. Conversion of pitch to oils and tar acids by degradative hydrogenation seems, on the basis of present knowledge, to be almost as difficult a technical and economic problem as hydrogenation of coal itself. Knowledge of the structure of the compounds that constitute the pitch fraction is incomplete, and such questions as to whether the pitches are largely primary or secondary products are still highly controversial. Almost no information is available on the kinds of bonds that must be broken to convert pitch to useful low-boiling components. The solution of these problems would appear to lie in programs that combine detailed characterization of components and systematic empirical experimentation.

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BIBLIOGRAPHY

1. DAVIS, J. D. Low-Temperature Tar and Its Evaluation. Am. Gas Assoc., Tech. Sec., vol. 4, 1922, pp. 65-76.

2. DAVIS, J. D., AND PARRY, V. F. Low-Temperature Carbonization of Pennsylvania Coals - Pittsburgh and Upper Kittanning Beds. Carnegie Inst. Technol. (and Bureau of Mines) Bull. 8, 1923, 56 pp.

3. BROWN, R. L., AND COOPER, R. B. What Oils Can Be Obtained From Coal by Low-Temperature Distillation and What Will Be Their Commercial Uses? Coal Age, vol. 26, 1926, pp. 905-906.

4. BROWN, R. L. Composition of Light Oils From Low-Temperature Carbonization of Utah Coal. Ind. Eng. Chem., vol. 19, 1927, pp. 26-31.

5. FIELDNER, A. C. Low-Temperature Carbonization of Coal. Bureau of Mines Tech. Paper 396, 1926, 46 pp.

6. BROWN, R. L., AND BRANTING, B. F. Composition of Tar From Low-Temperature Carbonization of Utah Coal. I. Ind. Eng. Chem., vol. 20, 1928, pp. 392-396.

7. DAVIS, J. D. Bibliography on Low-Temperature Tar, 1927 to Date. Proc. Am. Gas Assoc. 1928, pp. 1196-1197.

8. BROWN, R. L., AND POLLACK, R. N. Composition of Tar From Low-Temperature Carbonization of Utah Coal. II. Ind. Eng. Chem., vol. 21, 1929, pp. 234-238.

9. SCHNEIDER, E. J., AND SHOHAN, J. B. Xylenols and Higher Phenols That Have Been Found in Primary Tars. Bureau of Mines Rept. of Investigations 2968, 1929, 20 pp.

10. _____. Phenoxy Acetic Acids From Low-Temperature Tar. Bureau of Mines Rept. of Investigations 2969, 1929, 10 pp.

11. DAVIS, J. D., AND IREY, K. M. Study of Wax From Low-Temperature Tar. Ind. Eng. Chem., vol. 23, 1931, pp. 186-189.

12. KESTER, E. B., AND POHLE, W. D. Composition of the Fractions of Primary and High-Temperature Tar. Bureau of Mines Rept. of Investigations 3197, 1932, 11 pp.

13. KESTER, E. B., AND DAESCHNER, H. W. Composition of Low-Temperature Tars: V. Isolation and Identification of Certain Alcohols. Carnegie Inst. Tech. (and Bureau of Mines) Bull. 54, 1932, 32 pp.

14. FISCHER, C. H. Composition of Coal Tar and Light Oil. Bureau of Mines Bull. 412, 1938, 70 pp.

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15. PARRY, V. F. Correlation of Analysis of Coal With Products of Carbonization in Externally Heated Retorts. Bureau of Mines Rept. of Investigations 3482, 1939, 37 pp.

16. FIELDNER, A. C., DAVIS, J. D., PARRY, V. F., SCHMIDT, L. D., ELDER, J. L., GOODMAN, J. B., LANDERS, W. S., AND GOODWIN, E. W. Tests of the Heliopore Coal-Carbonization Power-Plant Process. Bureau of Mines Rept. of Investigations 3733, 1943, 36 pp.

17. ODE, W. H., AND SELVIG, W. A. Low-Temperature Distillation Yields of Primary Tar and Light Oil From Coals of Various Ranks and Types. Bureau of Mines Rept. of Investigations 3748, 1944, 10 pp.

18. SELVIG, W. A., ODE, W. H., AND DAVIS, J. D. Low-Temperature Carbonization of Alaskan Coals. Bureau of Mines Tech. Paper 668, 1944, 16 pp.

19. REID, W. T. Low-Temperature Carbonization of Coal in Japan. Bureau of Mines Inf. Circ. 7430, 1948, 82 pp.

20. PARRY, V. F. Résumé of Bureau of Mines Research and Development Work on Western Coals, 1942-47. Bureau of Mines Rept. of Investigations 4171, 1948, 9 pp.

21. BROWN, R. L., DAVIS, J. D., REYNOLDS, D. A., AND SMITH, F. W. Carbonizing Properties of American Coals: Index of Coals Tested by the Bureau of Mines. Bureau of Mines Bull. 536, 1954, 17 pp.

22. PARRY, V. F., LANDERS, W. S., WAGNER, E. O., GOODMAN, J. B., AND ALLEN, R. R. Utilization of South Arcot, India, Lignite. Bureau of Mines Rept. of Investigations 5351, 1957, 34 pp.

23. SELVIG, W. A., AND ODE, W. H. Low-Temperature Carbonization Assays of North American Coals. Bureau of Mines Bull. 571, 1957, 56 pp.

24. GOODMAN, J. B., GOMEZ, MANUEL, PARRY, V. F., AND LANDERS, W. S. Low-Temperature Carbonization Assay of Coal in a Precision Laboratory Apparatus. Bureau of Mines Bull. 530, 1953, 24 pp.

25. PARRY, V. F., LANDERS, W. S., WAGNER, E. O., GOODMAN, J. B., AND LAMMERS, G. C. Drying and Carbonizing Fine Coal in Entrained and Fluidized State. Bureau of Mines Rept. of Investigations 4954, 1953, 43 pp.

26. PARRY, V. F. Low-Temperature Carbonization of Coal and Lignite for Industrial Uses. Bureau of Mines Rept. of Investigations 5123, 1955, 27 pp.

27. GOMEZ, MANUEL, GOODMAN, J. B., AND PARRY, V. F. Changes Induced in Low-Temperature Tar by Oxidation and Storage. Bureau of Mines Rept. of Investigations 5227, 1956, 12 pp.

28. _____. Effects of Oxidation on Carbonization Yields of a Texas Lignite. Bureau of Mines Rept. of Investigations 5277, 1956, 17 pp.

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29. GOMEZ, MANUEL, GOODMAN, J. B., AND PARRY, V. F. Low-Temperature Tar From Fluidized Carbonizing Reactors. Bureau of Mines Rept. of Investigations 5302, 1957, 44 pp.

30. LOWRY, H. H., LANDAN, H. G., AND NAUGLE, L. L. Correlation of the Bureau of Mines-American Gas Association Carbonization Assay Tests With Coal Analyses. Trans. AIME, vol. 149, 1942, pp. 297-330.

31. ODE, W. H., AND SELVIG, W. A. Low-Temperature Distillation Yields of Primary Tar and Light Oil From Coals of Various Ranks and Types. Bureau of Mines Rept. of Investigations 3748, 1949, 10 pp.

32. PARRY, V. F., LANDERS, W. S., AND WAGNER, E. O. Low-Temperature Carbonization of Lignite and Non-Coking Coals in the Entrained State. Min. Eng., vol. 8, 1956, pp. 54-64.

33. HOEPPNER, J. J., OPLAND, M. L., AND FOWKES, W. W. Carbonization Characteristics of Some North-Central United States Lignites. Bureau of Mines Rept. of Investigations 5260, 1956, 21 pp.

34. KARR, C., JR., ESTEP, P. A., AND PAPA, A. J. Infrared Spectral-Structural Correlations of Quinolines. Am. Chem. Soc., Div. of Organic Chem., San Francisco meeting, April 1958.

35. KARR, C., JR. Physical Properties of Low-Boiling Phenols. A Literature Survey. Bureau of Mines Inf. Circ. 7802, 1957, 15 pp.

36. CHANG, YI-CHUNG. Potentiometric Titration of Free Amine and Amine Carbonate in Carbonated Monoethanolamine Solutions. Anal. Chem., vol. 30, 1958, pp. 1095-1097.

37. ANALYTICAL CHEMISTRY. Laboratory of the Month - Coal Tar Research Challenges Analysts. Vol. 29, No. 1, 1957, pp. 51A-53A.

38. KARR, C., JR., AND BROWN, P. M. Retention Volumes of Phenol, Methyl- and Dimethylphenols in Gas-Liquid Partition Chromatography. Am. Chem. Soc., Div. of Gas and Fuel Chem., Atlantic City meeting, September 1956.

39. KARR, C., JR., BROWN, P. M., ESTEP, P. A., AND HUMPHREY, G. L. Identification and Determination of Low-Boiling Phenols in Low-Temperature Coal Tar. Am. Chem. Soc., Div. of Gas and Fuel Chem., New York meeting, September 1957.

40. _____. Analysis of Low-Temperature Tar Phenols Boiling up to 234° C. Fuel, vol. 37, 1958, pp. 227-235.

41. CHANG, TA-CHUANG LO, AND KARR, C., JR. Ultraviolet Spectrophotometric Determination of Total Pyridines and Quinolines in Low-Temperature Coal-Tar Distillates. Anal. Chem., vol. 30, 1958, pp. 971-972.

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42. CHANG, TA-CHUANG LO, AND KARR, C., JR. Spectrophotometric Determination of Small Quantities of Some Individual Pyridine Bases by Successive Extractions. Anal. Chem., vol. 29, 1957, pp. 1617-1619.

43. HUNTER, J. G., AND HASH, A. W. A Study of the Principles of Solvent Extraction Processes for the Refining of Oil. World Petrol. Cong., London, proc. 2, 1933, pp. 340-350.

44. GOMEZ, MANUEL, GOODMAN, J. B., AND PARRY, V. F. General Properties of Low-Temperature Tar. Bureau of Mines Bull. 569, 1958, 31 pp.

45. COAL TAR RESEARCH ASSOCIATION (Leeds, England). The Coal-Tar Data Book. Sec. B, 1953.

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